

UNION OF SOVIET SOCIALIST  
REPUBLICS

(19) SU (11) 1,134,572 A

[Coat of Arms]

4 (51)

C 08 G 18/14

STATE COMMITTEE OF THE U S S R  
FOR INVENTIONS AND DISCOVERIES

SPECIFICATION OF INVENTION  
TO INVENTORS' CERTIFICATE

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(21) 3545517/23-05

(22) 26/01/83

(46) 15/01/85. Bull. No. 2

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(53) 678.664 (088.8)

(56) (1) Singer P.A., et. al. Production and  
properties of polycarbodiimide - base foam  
plastics. Chemistry and Technology of  
Polyurethanes. Moscow, 1977, p. 97.

(2) US Patent No. 4,166,164; Cl. 521-129;  
Published 1979 (Prior Art)

(54) (57) METHOD OF PRODUCING A FOAM MATERIAL WITH  
CARBODIIMIDE AND ISOCYANURATE GROUPS including simultaneous  
condensing and trimerisation of an isocyanate in the  
presence of a catalyst of the forming of carbodiimide  
groups and of an alkali metal carboxylate dissolved in a  
hydroxyl-containing compound, and of an organosilicon  
stabiliser, characterised in that, in order to enhance  
the strength ratings of the target product, used as the  
catalyst of the forming of carbodiimide groups is a

solution of 0.001 to 0.100 weight equivalent of an N-oxide of tertiary amine per 1 weight equivalent of isocyanate in 0.01 to 0.50 weight equivalent of the hydroxyl-containing compound, with 0.1 to 10.0 weight equivalents of the alkali metal carboxylate taken per 1 weight equivalent of the N-oxide of tertiary amine.

The invention relates to the production of foam materials having carbodiimide and isocyanurate groups, and it can be utilised in construction, general engineering, shipbuilding and aircraft engineering.

There is known a method of production of a foam material having carbodiimide groups, including condensing of isocyanate in the presence of catalysts of carbodiimide formulation, such as alkyl- or aryl phospholene oxides [1].

Foam polycarbodiimides produced by this known method are characterised by their low density and strength, and their open porosity.

To improve the properties of this polycarbodiimide, the latter is additionally thermally treated following the foaming.

The closest prior art of the present invention by the technical essence is the method of preparation of foam materials having carbodiimide and isocyanurate groups, including simultaneous condensing and trimerisation of an isocyanate in the presence of a catalyst of the forming of carbodiimide groups and of an alkali metal carboxylate, dissolved in a hydroxyl-containing compound, and of an organosilicon foam stabiliser [2].

Employed as the catalyst promoting the forming of carbodiimide groups are alcohols, amino alcohols, and derivatives of triazine and phospholene oxide.

The foam materials thus obtained, containing in their structure both carbodiimide and isocyanurate groups are characterised by a higher strength than a foam material

having carbodiimide groups alone. Hence, they do not require additional thermal treatment.

However, when the catalysts employed are in the form of combinations of alcohols, amino alcohols and triazine derivatives with alkali metal carboxylates, the forming of carbodiimides takes place solely as an auxiliary process. The content of carbodiimide groups in such foams is all but insignificant, so that the properties of the foams are not unlike those of purely isocyanurate foams, with no distinguishable advantages over the latter. With phospholene oxides employed as the catalyst promoting the forming of carbodiimide, foams with a high content of carbodiimide groups in the material can be prepared. In this case, however, the strength of the foams obtained is lower than that of polyurethane and polyisocyanurate foams of the same density, while the toxicity of phospholene oxides introduces a toxicity hazard of the process of production of the foams and of the foams themselves.

It is an object of the present invention to enhance the strength ratings of the target product.

This object is attained in a method of producing a foam material with carbodiimide and isocyanurate groups, including simultaneous condensing and trimerisation of isocyanate in the presence of a catalyst of the forming of carbodiimide groups and of an alkali metal carboxylate, dissolved in a hydroxyl-containing compound, and of an organosilicon stabiliser, the catalyst used to promote the forming of carbodiimide groups being a solution of 0.001 to 0.100 weight equivalent of an N-oxide of tertiary amine per 1 weight equivalent of isocyanate in 0.01 to 0.50 weight equivalent of the hydroxyl-containing compound, with 0.1 to

10.0 weight equivalents of the alkali metal carboxylate taken per 1 weight equivalent of the N-oxide of tertiary amine.

Employed as the hydroxyl-containing compound are low-molecular alcohols, polyether polyols or polyester polyols, epoxy resins, phenol formaldehyde resins, or their blends.

Like other organophosphorus compounds, phospholene oxides used as the catalysts promoting the forming of carbodiimide are toxic. They are not converted at the foaming stage, and are gradually released in the course of the use of the foams, this release being accelerated by elevated temperatures which also bring about the hazard of their decomposition, with even more toxic phosphines yielded. The use of N-oxides of tertiary amines as the catalyst of the forming of carbodiimides, with their not only lower volatility (owing to their salt nature) but also lower toxicity (thus, tert-methylamine oxide is contained in fish and in live tissues) makes the foaming process and the target foam material itself significantly less toxic. Virtually complete elimination of toxicity can be attained by the use of N-oxides of hydroxyl-containing tertiary amines, such as N,N-dimethylethanolamine oxide, N-ethyltriethanolamine oxide, triethanolamine oxide, and other like compounds. These oxides become securely bound by the isocyanate at the foaming stage, and would not be released in the forthcoming use.

The higher strength of the foams is an outcome of the specific ratios of the rates of carbodiimide formulation, with its accompanying evolution of gas and trimerisation bringing about cross-linking of the polymer. In this, the N-oxides of tertiary amines not only serve as the catalysts of

the forming of carbodiimide, but also act as a cocatalyst of trimerisation of isocyanate jointly with carboxylates.

The ratio of the carbodiimide and isocyanurate groups in the polymer is controlled by varying the ratios of the added N-oxide of tertiary amine, alkali metal carboxylate and hydroxyl-containing compound.

The control over the foaming parameters is achieved by varying the total content of the catalysts in the compounding, or else by adding carboxylic acids, preferably those whose alkaline salts are employed as the catalyst in the compounding selected. These acids slow down the foaming the greater, the bigger is their added amount.

The catalysts of the forming of carbodiimides in this method are N-oxides of aliphatic (trimethylamine, triethyl amine, N,N-dimethylethanolamine, triethanolamine and the like), alicyclic ((N,N-dimethylcyclohexyl amine, N-methylcyclohexyl amine, N,N-dimethylcyclopentyl amine and the like) and heterocyclic (N-methyl piperidine, N-ethanol piperidine, N,N'-dimethyl piperazine, N-methyl pyrrolidine, triethylene diamine and the like) tertiary amines. However, oxides of aromatic nitrogen-containing heterocyclic compounds and of aromatic tertiary amines, such as pyridine oxide and N,N-dimethylaniline oxide are weak catalysts of the forming of carbodiimide, and their use is ill-advised. With all of the oxides of tertiary amines being hygroscopic substances and their complete dehydration being more often than not highly complicated, in some cases use of their hydrates appears to be more convenient.

The catalysts of trimerisation of isocyanate in the disclosed method are lithium, sodium and potassium salts of

mono- and dicarboxylic acids, such as formic, acetic, propionic, butyric, lactic, oleic, succinic, tartaric and like acids.

The alkali metal carboxylate and the N-oxide of tertiary amine are dissolved prior to the foaming stage either in a low-molecular alcohol, or in a polyether polyol or a polyester polyol, or in an epoxy resin, or in a phenolformaldehyde resin, or else in a blend of the listed hydroxyl-containing compounds.

Used as the low-molecular alcohol are either monohydric or polyhydric alcohols, such as methanol, ethanol, butanol, methyl cellosolve [sic!], ethylene glycol, diethylene glycol, propylene glycols, butanediols, glycerin, etc.

Used as the polyether polyols are products of oxyalkylation of polyhydric alcohols, or else of carbohydrates or amines.

Used as the polyester polyols are products of reaction of polyhydric alcohols with carboxylic acids.

Used as the epoxy resins are products of reaction of epichlorohydrin with diphenylpropane or with other compounds having mobile hydrogen atoms.

Used as the phenolformaldehyde resins are liquid products of condensing of phenol or its derivatives with formaldehyde.

Good results are derived from the use of blends of the hydroxyl-containing compounds listed above, e.g. of a low-molecular alcohol with a polyether polyol or a polyester polyol, of an epoxy resin with a polyether polyol, or of a phenolformaldehyde resin with a polyether polyol, and so on.

As many alkali metal carboxylates are poorly soluble in polyether polyols or polyester polyols, in epoxy resins or in phenolformaldehyde resins, it is more convenient to dissolve them in advance in a low-molecular alcohol, water or a blend of water and an alcohol, and only subsequently have them mixed with said hydroxyl-containing compounds.

When significant amounts of hydroxyl-containing compounds are used, except N-oxides and alkali metal carboxylates, the compounding may have added to it generally employed catalysts of the forming of urethanes, e.g. tertiary amines, tin or organometallic compounds.

In accordance with the disclosed method, foam materials having carbodiimide and isocyanurate groups can be prepared with the use of isocyanates with functionality of 2, such as isomers of toluylene diisocyanate, 4,4"-diphenylmethane diisocyanate, polyisocyanate, and also of various prepolymers terminating in isocyanate groups.

The foaming of the materials takes place owing to the release of carbon dioxide in the forming of the carbodiimide; however, if required, generally employed foaming agents can be used, e.g. water or halogen hydrocarbons.

In the preparation of foams, highly effective foam stabilisers are organosilicon ones, e.g. a block polymer of polyorganosiloxane and polyoxyalkylene.

To step up fire resistance of the carbodiimide and isocyanurate group-containing materials being produced, there are added commonly employed fireproofing compounds of the additive kind, e.g. tris(2-chloroethyl) phosphate,



tris(2-chloropropyl) phosphate, or aluminium hydroxide. Of special effect is joint addition of tris(2-chloroethyl) phosphate and starch, which allows fire-resistant foams retaining their dimensions when charred or subjected to open flame to be obtained.

The production of foams by the disclosed method is conducted as follows.

An alkali metal carboxylate and an N-oxide of tertiary amine are dissolved in a hydroxyl-containing compound or in a blend of hydroxyl-containing compounds. Introduced into this mixture are a foam stabiliser, a foaming agent (if required), and special additives (fireproofing compounds, fillers, dyes, plasticisers, and so on). These special additives alternatively can be introduced into the isocyanate component. The polyol and isocyanate components thus prepared can be stored for prolonged periods and blended directly prior to the foaming stage. The processing of this twin-component system into a foam material can be performed in the conventional equipment intended for processing of polyurethane compositions by either moulding or spray deposition.

Example 1. Dissolved in a 300 ml vessel are 5.48 grams (0.056 gram equivalent - g eq) potassium acetate and 5.48 g (0.059 g eq) hydrate of trimethylamine N-oxide in 5.48 g ethylene glycol. Then 2.0 g KEP-2 foam stabiliser is added to the solution thus prepared, and agitated. Upon the addition of 137.0 g polyisocyanate (1 g eq) and agitation for 5 seconds, the blend foams up.

Example 2. Similarly to Example 1, a solution of 3.88 g (0.0396 g eq) potassium acetate and 3.88 g (0.0717 g eq) and

hydrate of trimethylamine oxide in 3.88 g (0.125 g eq) ethylene glycol is mixed with 30.0 g ED-20 epoxy resin, 10.0 g tris(2-chloroethyl) phosphate, 2.0 g KEP-2 and 137.0 g polyisocyanate (with 30.6 % content of NCO groups).

Example 3. Similarly to Example 1, a solution of 0.98 g (0.01 g eq) potassium acetate and 3.0 g (0.0256 g eq) N,N"-dioxytetraethyl diaminoisopropanol in 2.4 g (0.077 g eq) ethylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 4. Similarly to Example 1, a solution of 0.98 g (0.01 g eq) potassium acetate and 3.0 g (0.021 g eq) of N-oxide of N-butyl pyrrolidone in 2.4 g (0.077 g eq) ethylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 5. Similarly to Example 1, a solution of 0.98 g (0.01 g eq) potassium acetate and 2.8 g (0.039 g eq) triethyleneamine N,N'-dioxide in 3.1 g (0.1 g eq) ethylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 6. Similarly to Example 1, a solution of 0.98 g (0.01 g eq) potassium acetate and 3.0 g (0.02 g eq) N-ethyldiethanolamine N-oxide in 2.4 g (0.077 g eq) ethylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 7. Similarly to Example 1, a solution of 2.85 g (0.0291 g eq) potassium acetate and 2.85 g (0.0248 g eq) N,N'-dibutyl piperazine N,N'-dioxide in 5.7 g (0.15 g eq) propylene glycol is mixed with 11.5 g tris(2-chloroethyl) phosphate, 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 8. Similarly to Example 1, a solution of 0.98 g (0.01 g eq) potassium acetate and 0.143 g (0.001 g eq) N-butyl pyrrolidine in 7.6 g (0.1 g eq) methyl cellosolve is mixed with 30.0 g ED-2 epoxy resin, 25.0 g (0.156 g eq) oxypropylated xylite (Laprol -805V), 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 9. Similarly to Example 1, a solution of 0.98 g (0.01 g eq) potassium acetate and 21.1 g (0.1 g eq) N-benzyl diethanolamine N-oxide in 20.0 g (0.377 g eq) diethylene glycol with 30.0 g (0.187 g eq) Laprol -805V, 50.0 g (0.05 g eq) Laprol -3003, 3.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 10. Similarly to Example 1, a solution of 2.47 g (0.03 g eq) potassium acetate and 2.74 g (0.023 g eq) triethylamine N-oxide in 15.5 g (0.5 g eq) ethylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 11. Similarly to Example 1, a solution of 2.2 g (0.0225 g eq) potassium acetate and 2.74 g (0.0234 g eq) triethylamine N-oxide in 20.0 g (0.22 g eq) 1,4-butylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 12. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 13. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.56 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 13.7 g ED-20 epoxy resin and 137.0 g (1 g eq) polyisocyanate.

Example 14. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 13.7 g Laprol -805V, and 137.0 g (1 g eq) polyisocyanate.

Example 15. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 27.4 g (0.17 g eq) Laprol -805V and 137.0 g (1 g eq) polyisocyanate.

Example 16. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 2.5 g (0.042 g eq) acetic acid and 137.0 g (1 g eq) polyisocyanate.

Example 17. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 137.0 g (0.043 g eq) polyethylene glycol adipate and 137.0 g (1 g eq) polyisocyanate.

Example 18. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 7.02 g (0.06 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol

is mixed with 2.0 g KEP-2 and 137.0 g (1 g eq) polyisocyanate.

Example 19. Similarly to Example 1, a solution of 1.96 g (0.02 g eq) potassium acetate and 2.34 g (0.02 g eq) triethylamine N-oxide in 4.58 g (0.147 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 20.0 g FRB-1A phenolformaldehyde resin and 137.0 g (1 g eq) polyisocyanate.

Example 20. Similarly to Example 1, a solution of 0.75 g (0.0077 g eq) potassium acetate and 0.9 g (0.0077 g eq) triethylamine N-oxide in 1.5 g (0.05 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 16.0 g (0.1 g eq) Laprol -805V, 16.0 g ED-20 epoxy resin, 16.0 g tris(2-chloroethyl) phosphate and 137.0 g (1 g eq) polyisocyanate.

Example 21. Similarly to Example 1, a solution of 1.5 g (0.0153 g eq) potassium acetate and 1.8 g (0.0153 g eq) triethylamine N-oxide in 3.5 g (0.113 g eq) ethylene glycol is mixed with 2.0 g KEP-2, 16.0 g ED-20 epoxy resin, 16.0 g tris(2-chloroethyl) phosphate, 1.7 g (0.028 g eq) acetic acid and 137.0 g (1 g eq) polyisocyanate.

The foaming parameters and physical/mechanical properties of the foam materials thus prepared are summed up in the table below.

Example 22 (control). Similarly to Example 1, a solution of 0.59 g (0.006 g eq) potassium acetate and 0.7 g (0.006 g eq) triethylamine N-oxide in 1.35 g (0.0436 g eq) ethylene glycol is mixed with 2.0 g OP-7, 53.0 g tall oil, 22.0 g triethanolamine, 15.0 g tris(2-chloroethyl) phosphate, and 137.0 g (1 g eq) polyisocyanate.

For comparison sake, let us consider the data on the strength of isocyanurate /carbodiimide materials having 50 % and 30 % carbodiimide groups (in terms of the initial NCO groups). As per the source of the prior art, with the density of 20 kg/m<sup>3</sup> the isocyanurate-carbodiimide foam plastic (50 % carbodiimide groups in terms of NCO) has the compression strength of 0.06 MPa, and with the density of 47 kg/m<sup>3</sup>, the foam plastic (30 % carbodiimide groups in terms of NCO), the compression strength of 0.18 MPa. With about the same density and content of carbodiimide groups, foam materials produced by the disclosed method offer the strength of 0.11 MPa (Example 1, the foam material density of 16.3 kg/m<sup>3</sup>) and 0.24 MPa (Example 12, the foam material density of 43.5 kg/m<sup>3</sup>), i.e. by 83 % and 33 % higher, respectively.

Thus, the disclosed method enables production of foam materials of a high specific strength, in a broad range of densities. These materials are different to polyisocyanurate ones by their absence of brittleness, while differing from their polyurethane counterparts by the higher heat- and fire resistance.

The broad versatility of the disclosed catalyst system allows most various hydroxyl-containing initial materials to be used, and both rigid and semi-rigid foams to be prepared.

The replacement of expensive and scarce phospholene oxides with less scarce and less expensive N-oxides of tertiary amines results in a significantly lower production cost of carbodiimide-isocyanurate foams, in addition to their lower toxicity and the facilitated technology of their fabrication.

Example	Starting Time s	Foam Rising Time, s	Apparent Density of Foam Materials, kg/m <sup>3</sup>	Compression Strength, MPa
1	2	3	4	5
1	6	15	16.3	0.11
2	6	25	19.1	0.07
3	15	110	71.5	0.74
4	6	35	88.7	0.86
5	20	50	65.1	0.45
6	12	135	63.7	0.40
7	6	30	34.1	0.16
8	15	25	187.2	3.81
9	3	9	62.3	0.10
10	12	30	38.1	0.15
11	11	80	44.5	0.20
12	5	15	43.5	0.24
13	6	25	58.0	0.43
14	7	30	47.6	0.31
15	8	38	55.3	0.29
26	12	50	21.3	0.12
27	7	25	43.2	0.21
18	3	10	14.8	0.08
19	6	40	47.0	0.15
20	7	30	82.6	0.79
21	13	60	42.8	0.26
22	10	45	151.3	2.63